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## EP 1 104 801 A1

## Description

5 [0001] The present invention relates to a particulate detergent and cleaning composition containing surfactants and bleaching agents, optionally together with other conventional ingredients.

[0002] Detergent and cleaning compositions have already been described on many occasions in the literature and normally contain surfactants, builders and frequently bleaching agents and/or enzymes as well. Bleaching agents and enzymes act specifically on so-called bleachable soiling or, respectively, on enzymatically removable soiling. Both bleaching agents and enzymes lose a large part of their activity on storage. Bleaching agents, which conventionally are peroxide-containing substances, are particularly unstable towards water, including atmospheric moisture, and decompose slowly into the corresponding oxides, thereby reducing the bleaching activity.

[0003] Enzymes are e.g. temperature-sensitive and lose a substantial part of their enzyme activity on storage if bleaching agents are present.

[0004] In the development of novel detergent and cleaning compositions, considerable effort has been made to increase the washing activity of the compositions. However, the increase in washing activity can normally only be observed for a short time after production because the activity decreases substantially over time after prolonged storage, due to the interactions described above.

25 [0005] German patent application DE 196 51 446 describes enzyme granules suitable for incorporation into particulate detergent and cleaning compositions, said granules containing enzymes and an inorganic and/or organic carrier and having a uniform outer sheathing layer containing pigments. The sheathing layer consists of a sheathing system containing 5% by weight to 70% by weight of a finely divided, water-insoluble pigment, 45% by weight to 90% by weight of a water-soluble

organic substance solid at room temperature and melting in the range from 40°C to 70°C, and up to 20% by weight of a flowability improver.

[0006] German patent application DE 196 44 244 describes a process for coating temperature-sensitive granules in a fluidized bed apparatus, wherein a fusible coating material is used and the molten coating material, kept at a temperature at least 20°C above the melting point, is sprayed with atomizing air, which is at least at the same temperature, through nozzles into a fluidizing chamber filled with the granules to be coated, the outer jacket being kept at a temperature of 20 to 50°C.

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[0007] The object of the present invention was to provide a storage-resistant detergent and cleaning composition in solid form, containing bleaching agents, which is resistant to storage over a long period, i.e. the activity of sensitive substances scarcely decreases, if at all, over this period.

[0008] Surprisingly, it has been found that if the particles of particulate detergent and cleaning compositions are at least partially provided with a protective coating, the activity of the sensitive substances, and hence the washing activity overall, is maintained even over long storage periods.

[0009] Accordingly, the present invention provides a particulate detergent and cleaning composition containing surfactants, bleaching agents and optionally other conventional ingredients, which is characterized in that the particles are at least partially provided with a protective layer.

[0010] The particulate detergent and cleaning compositions according to the present invention can take the form of powders, granules, extrudates or mouldings, including tablets in particular. The individual particulate constituents can have a homogeneous composition or they can be a mixture of different particulate constituents.

[0011] In terms of the present invention, the expression "the particles are at least partially provided with a protective layer" means that either all or only some of the particles present in the whole composition have such a protective layer, independently of whether said composition consists of homogeneous particles (solids) or a mixture of different particles which together form the finished

The washing activity is maintained detergent and cleaning composition. particularly well if at least 65% of the particles present in the composition are provided with a protective layer. The thickness of the protective layer is preferably  $0.1 \, \mu m$  to  $100 \, \mu m$ .

[0012] Particularly suitable coating compositions for forming the protective layer 5 according to the invention are substances and mixtures of substances which are solid at room temperature, especially those melting in the range from 40°C to 200°C. Particularly preferably, 50% by weight to 100% by weight of the protective layer is made up of water-soluble organic substances melting in said range.

[0013] Water-soluble substances which are particularly preferably used within 10 the framework of the present invention are understood as meaning substances that dissolve in water to the extent of at least 50 g/l, particularly at least 80 g/l, at a temperature of 30°C. These water-soluble substances can constitute up to 100% of the protective layer.

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[0014] The water-soluble substance solid at room temperature, which preferably forms the main component of the sheathing protective layer, is selected especially from non-ionic surfactants, such as alkoxylated alcohols, fatty acids, fatty acid amides and/or hydroxy fatty acid esters. It is preferably an alcohol, especially a linear primary alcohol having 16 to 22 C atoms, etherified with an average of 45 to 120, especially 60 to 110, mol equivalents of an alkylene oxide, especially ethylene oxide. Said alcohols include particularly stearyl alcohol, arachidyl alcohol, behenyl alcohol and monounsaturated to triunsaturated alcohols of corresponding chain length, it being essential for said alkoxylated alcohol component to melt in the range from 40°C to 200°C, especially 50°C to 70°C, this being understood as meaning the temperature at which 100% of the substance is present in liquid form on heating. As an alternative to the alcohol ethoxylates, or in addition thereto, it is also possible to use ethoxylated fatty acids, ethoxylated fatty acid amides and/or ethoxylation products of hydroxy fatty acid esters having 1 to 6 C atoms in the alcohol moiety of the ester, for example ricinoleic acid glyceride, the degree of ethoxylation in each case being preferably 45 to 120, especially 60 to 110. The 30

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fatty acid component of said substances has preferably 12 to 22 C atoms, especially The alkoxylates preferred in this connection include 16 to 18 C atoms. ethoxylation products said to have a narrow distribution of homologues (nre = narrow range ethoxylates), such as those obtained by the process of European patent EP 339 426 or international patent application WO 90/13533. If desired, the ethoxy groups in said alkoxylation products can be at least partially replaced by propoxy groups. When using mixtures of substances, it is also possible to use those containing small proportions, normally below 15% by weight, based on the mixture, of components liquid at room temperature, provided that the overall mixture appears solid at room temperature and has a solidification point ranging from 40°C to 200°C, especially 50°C to 70°C. The solidification point is the temperature at which solidification occurs when a material heated to a temperature It can be determined with a rotating above the melting point is cooled. thermometer by the method of DIN ISO 2207. Particularly suitable substances for the preparative process according to the invention are those which, when mixed with the other components of the sheathing system, give a melt of greatest possible homogeneity which can be sprayed at temperatures of up to 120°C. As an indication in this connection, liquids with viscosities of up to about 500 mPas at said temperatures can normally be sprayed and applied to enzyme granules without difficulty by means of devices intended for this purpose, such as those known e.g. from German patent application 196 44 244.

[0015] Other constituents which the protective layer can contain are water-insoluble inorganic components, flowability improvers and organic dyestuffs.

[0016] The water-insoluble inorganic components which can be used in the protective layer, if desired in amounts preferably of 10% by weight, include e.g. inorganic pigments such as calcium carbonate, titanium dioxide, which can be present in the rutile or anatase crystalline modification, zinc oxide, zinc sulfide, white lead (basic lead carbonate), barium sulfate, aluminium hydroxide, antimony oxide, lithopone (zinc sulfide/barium sulfate), kaolin, chalk, talcum and/or mica. These are present in a sufficiently finely divided form that they can be dispersed in

a melt of the other constituents of the coating system intended for the formation of the protective layer. The mean particle size of such pigments conventionally ranges from 0.004  $\mu m$  to 50  $\mu m$ . It is also possible to use pigments surface-modified with dispersants. It is preferable to use titanium dioxide pigment, especially in rutile form, surface-modified with Al, Si, Zr or polyol compounds, such as that marketed e.g. under the trade name Kronos® 2132 (Kronos-Titan) or Hornbitan® R 522 (Sachtleben Chemie GmbH). It is also possible to use AG or VC grades of Tiona® RLL from Solvay and RD, R-KB and AZ grades of Bayertitan® from Bayer AG.

[0017] Other suitable components of the coating system intended for the formation of the protective layer are flowability improvers, if desired in amounts preferably of up to 10% by weight of the protective layer. Flowability improvers are understood as meaning active ingredients whose absence results in an impairment of the flowability of the sheathed granules. Examples of flowability improvers which can be used are aluminium silicates, zeolites, sodium silicates or silicic acids, which can be homogeneously mixed in finely divided form with the other constituents of the sheathing system for application to the enzyme granules, or can be applied separately after application of the other constituents.

[0018] The protective layer can also contain organic dyestuffs, particularly suitable dyestuffs being those which can be dissolved or suspended in water or in organic substances liquid at room temperature. By way of example, anionic dyestuffs, e.g. anionic nitroso dyestuffs, are suitable. One example of a possible dyestuff is naphthol green (Colour Index (CI) Part 1: Acid Green 1; Part 2: 10020), which is commercially available e.g. as Basacid® Grün 970 (CAS No. 19381-50-1) from BASF, Ludwigshafen, or mixtures thereof with suitable blue dyestuffs. Other dyestuffs which can be used are Pigmosol® Blau 6900 (CI 74160), Pigmosol® Grün 8730 (CI 74260), Basonyl® Rot 545 FL (CI 45170), Sandolan® Rhodamin EB400 (CI 45100), Basacid® Gelb 094 (CI 47005), Sicovit® Patentblau 85 E 131 (CI 42051), Acid Blue 183 (CAS 12217-22-0, CI Acid Blue 183), Pigment Blue 15 (CI 74160), Supranol® Blau GLW (CAS 12218-32-8, CI Acid Blue 221), Nylosan®

Gelb N-7GL SGR (CAS 61814-57-1, CI Acid Yellow 218) and/or Sandolan® Blau (CI Acid Blue 182, CAS 12219-26-0).

[0019] Other suitable dyestuffs are Ponceau 4R (CAS No. 2611-82-7, CI 16255), Allura Red 40 (CAS No. 25956-17-6, CI 16035), Aluminium Rot RLW (CI Mordant Red 83), Supranol® Rot GW (CAS No. 61901-44-8), Basantol® Rot 310 (CAS No. 61951-36-8), Supranol® Grün 6 GW (anthraquinone dyestuff formulation with Acid Green 81), Supranol® Grün BW (anthraquinone dyestuff formulation with Acid Green 84), Ultramarinblau 6394 (CAS No. 57455-37-5, CI 77007), Acid Yellow 17 (CAS No. 6359-98-4, CI 18965) and Acid Yellow 23 (CAS No. 1934-21-0, CI 19140).

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The substances known as optical brighteners, whose use in detergent and cleaning compositions is known from the state of the art, are also suitable. These substances are organic dyestuffs that convert part of the invisible UV radiation of sunlight into blue light of longer wavelength. They essentially belong to five structural groups, namely stilbenes, diphenylstilbenes, coumarins, quinolines and diphenylpyrazolines, and to the group in which benzoxazole or benzimidazole is combined with conjugated systems. A survey of common brighteners can be found e.g. in G. Jakobi, A. Löhr "Detergents and Textile Washing", VCH-Verlag, Weinheim, 1987, pages 94 to 100. Examples of suitable compounds are salts of 4,4'-bis[(4-anilino-6-morpholino-s-triazin-2-yl)amino|stilbene-2,2'-disulfonic acid or compounds of similar structure in which the morpholino group has been replaced by a diethanolamino group, a methylamino group, an anilino group or a 2methoxyethylamino group. Brighteners of the substituted biphenylstyryl type can also be present, examples being the alkali metal salts of 4,4'-bis(2sulfostyryl)biphenyl, 4,4'-bis(4-chloro-3-sulfostyryl)biphenyl or 4-(4-chlorostyryl)-4'-(2-sulfostyryl)biphenyl.

[0021] The above-mentioned dyestuffs can be used as one-coloured or multicoloured systems, individually or as mixtures.

[0022] In one preferred embodiment of the present invention, the protective layer consists of a sheathing system containing 45% by weight to 100% by weight of a

water-soluble organic substance solid at room temperature and melting in the range from 40°C to 200°C, up to 10% by weight, preferably up to 5% by weight and especially 0.5% by weight to 5% by weight of a finely divided, water-insoluble inorganic pigment, up to 20% by weight, preferably up to 10% by weight and especially 1% by weight to 5% by weight of a flowability improver and up to 1.5% by weight of an organic dyestuff.

[0023] In another embodiment, the sheathing system contains, as an additional component, small amounts, i.e. preferably 3% by weight to 10% by weight, especially 4% by weight to 8% by weight, of a compound of general formula I:

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## $R[O(C_nH_{2n}O)_mH]_x (I)$

in which R is an organic radical having 3 to 12 C atoms, especially 4 to 10 C atoms, n is 2 or 3, m is 1 to 15 and x is 2 or 3. Such components can be prepared in known manner by reacting alcohols R[OH]<sub>x</sub> with ethylene oxide and/or propylene oxide and can be part of the above-mentioned portion liquid at room temperature. Preferred compounds of general formula I include those which contain both ethoxy groups (n = 2) and 1,2-propoxy groups (n = 3), the average number of ethoxy groups per hydroxyl group of the alcohol R[OH]<sub>x</sub> preferably being up to 10 and the average number of propoxy groups per hydroxyl group of the alcohol R[OH]<sub>x</sub> preferably being up to 5. Of these compounds it is preferable to use those which have been prepared by reacting said alcohol firstly with propylene oxide and then with ethylene oxide. The preferred alcohols R[OH]<sub>x</sub> include 1,6-hexylene glycol, glycerol and trimethylolpropane.

[0024] In one preferred embodiment of the invention, the sheathing material system is a mixture of 0.5 to 5% by weight of a water-insoluble inorganic pigment, 10% by weight to 40% by weight, especially 15% by weight to 30% by weight, of the above-mentioned ethoxylated fatty acid, 15% by weight to 77% by weight, especially 27% by weight to 71% by weight, of the above-mentioned ethoxylated fatty alcohol and 3% by weight to 10% by weight, especially 4% by weight to 8%

by weight, of a compound of general formula I.

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[0025] The compositions sheathed according to the invention contain surfactants, e.g. non-ionic, anionic and amphoteric surfactants - apart from the surfactant portion optionally present in the protective layer - and bleaching agents, optionally together with other conventional ingredients.

The non-ionic surfactants preferably used are alkoxylated, advantageously ethoxylated, especially primary alcohols having preferably 8 to 18 C atoms and an average of 1 to 12 mol of ethylene oxide (EO) per mol of alcohol, in which the alcohol radical can be linear or, preferably, methyl-branched in the 2-position, or can consist of a mixture of linear and methyl-branched radicals, as is conventionally the case in oxoalcohol radicals. However, particularly preferred alcohol ethoxylates are those with linear radicals from alcohols of native origin having 12 to 18 C atoms, e.g. from coconut fatty alcohol, palm fatty alcohol, tallow fatty alcohol or oleyl alcohol, and an average of 2 to 8 EO per mol of alcohol. The preferred ethoxylated alcohols include e.g. C<sub>12-14</sub> alcohols with 3 EO or 4 EO, C<sub>9-11</sub> alcohols with 7 EO, C<sub>13-15</sub> alcohols with 3 EO, 5 EO, 7 EO or 8 EO, C<sub>12-18</sub> alcohols with 3 EO, 5 EO or 7 EO, and mixtures thereof, such as mixtures of a  $C_{12-14}$ alcohol with 3 EO and a C<sub>12-18</sub> alcohol with 5 EO. The indicated degrees of ethoxylation represent statistical mean values which can be an integer or a fraction for a specific product. Preferred alcohol ethoxylates have a narrow distribution of homologues (narrow range ethoxylates = NRE). In addition to these non-ionic surfactants, it is also possible to use fatty alcohols with more than 12 EO, examples being tallow fatty alcohol with 14 EO, 25 EO, 30 EO or 40 EO.

[0027] Another class of non-ionic surfactants that are preferably used, either individually or in combination with other non-ionic surfactants, consists of alkoxylated, preferably ethoxylated or ethoxylated and propoxylated, fatty acid alkyl esters preferably having 1 to 4 carbon atoms in the alkyl chain, especially fatty acid methyl esters.

[0028] Another class of non-ionic surfactants that can advantageously be used consists of alkyl polyglycosides. Alkyl polyglycosides which can be used

correspond to the general formula RO(G)<sub>z</sub>, in which R is a linear or branched, saturated or unsaturated aliphatic radical having 8 to 22 C atoms, preferably 12 to 18 C atoms, especially one which is methyl-branched in the 2-position, and G is the symbol representing a glycose unit having 5 or 6 C atoms, preferably glucose. The degree of glycosidation z is between 1.0 and 4.0, preferably between 1.0 and 2.0 and especially between 1.1 and 1.4. It is preferable to use linear alkyl polyglucosides, i.e. alkyl polyglycosides in which the polyglycosyl residue is a glucose residue and the alkyl radical is an n-alkyl radical.

[0029] Other suitable types of non-ionic surfactants are amine oxides, for example N-coconut fatty alkyl-N,N-dimethylamine oxide and N-tallow alkyl-N,N-dihydroxyethylamine oxide, and fatty acid alkanolamides. The amount of these non-ionic surfactants is preferably not greater than that of the ethoxylated fatty alcohols, especially not greater than half of the latter.

[0030] Other suitable surfactants are polyhydroxy fatty acid amides of formula 15 (II):

R<sup>1</sup> | R-CO-N-[Z] (II)

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in which RCO is an aliphatic acyl radical having 6 to 22 carbon atoms, R<sup>1</sup> is hydrogen or an alkyl or hydroxyalkyl radical having 1 to 4 carbon atoms and [Z] is a linear or branched polyhydroxyalkyl radical having 3 to 10 carbon atoms and 3 to 10 hydroxyl groups. Polyhydroxy fatty acid amides are known substances conventionally obtainable by reductive amination of a reducing sugar with ammonia, an alkylamine or an alkanolamine, followed by acylation with a fatty acid, a fatty acid alkyl ester or a fatty acid chloride.

[0031] The group of polyhydroxy fatty acid amides also includes compounds of formula (III):

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 $R^{1}$ -O- $R^{2}$  | R-CO-N-[Z] (III)

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in which R is a linear or branched alkyl or alkenyl radical having 7 to 12 carbon atoms, R<sup>1</sup> is a linear, branched or cyclic alkyl radical or an aryl radical having 2 to 8 carbon atoms, R<sup>2</sup> is a linear, branched or cyclic alkyl radical, an aryl radical or an oxyalkyl radical having 1 to 8 carbon atoms, C<sub>1-4</sub>-alkyl or phenyl radicals being preferred, and [Z] is a linear polyhydroxyalkyl radical whose alkyl chain is substituted by at least two hydroxyl groups, or alkoxylated, preferably ethoxylated or propoxylated, derivatives of this radical. [Z] is preferably obtained by reductive amination of a reduced sugar, for example glucose, fructose, maltose, lactose, galactose, mannose or xylose. The N-alkoxy-substituted or N-aryloxy-substituted compounds can then be converted to the desired polyhydroxy fatty acid amides by reaction with fatty acid methyl esters in the presence of an alkoxide as catalyst, for example according to the teaching of international patent application WO 95/07331.

[0032] Examples of anionic surfactants used are those of the sulfonate and sulfate types. Suitable surfactants of the sulfonate type are preferably  $C_{9-13}$ -alkylbenzenesulfonates, olefinsulfonates, i.e. mixtures of alkenesulfonates and hydroxyalkanesulfonates, and corresponding disulfonates, such as those obtained e.g. from  $C_{12-18}$  monoolefins with a terminal or internal double bond by sulfonation with gaseous sulfur trioxide, followed by alkaline or acidic hydrolysis of the sulfonation products. Other suitable sulfonates are alkanesulfonates obtained from  $C_{12-18}$  alkanes e.g. by sulfochlorination or sulfoxidation, followed by hydrolysis or neutralization. The esters of  $\alpha$ -sulfo fatty acids (ester sulfonates), e.g. the  $\alpha$ -sulfonated methyl esters of hydrogenated coconut fatty acid, palm kernel fatty acid or tallow fatty acid, are also suitable.

[0033] Other suitable anionic surfactants are sulfonated fatty acid glycerol esters.

Fatty acid glycerol esters are understood as meaning the monoesters, diesters and

triesters and mixtures thereof, such as those obtained by the esterification of a monoglycerol with 1 to 3 mol of fatty acid or by the transesterification of triglycerides with 0.3 to 2 mol of glycerol. Preferred sulfonated fatty acid glycerol esters are the sulfonation products of saturated fatty acids having 6 to 22 carbon atoms, for example caproic acid, caprylic acid, capric acid, myristic acid, lauric acid, palmitic acid, stearic acid or behenic acid.

[0034] Preferred alk(en)ylsulfates are the alkali metal salts and especially the sodium salts of the sulfuric acid half-esters of C<sub>12</sub>-C<sub>18</sub> fatty alcohols, for example coconut fatty alcohol, tallow fatty alcohol, lauryl alcohol, myristyl alcohol, cetyl alcohol or stearyl alcohol, or of C<sub>10</sub>-C<sub>20</sub> oxoalcohols, and the sulfuric acid half-esters of secondary alcohols of these chain lengths. Alk(en)ylsulfates of said chain length containing a synthetic linear alkyl radical prepared from petrochemicals, whose degradation behaviour is analogous to that of suitable compounds based on raw materials from fat chemistry, are also preferred. C<sub>12</sub>-C<sub>16</sub>-alkylsulfates, C<sub>12</sub>-C<sub>15</sub>-alkylsulfates and C<sub>14</sub>-C<sub>15</sub>-alkylsulfates are preferred where detergency is concerned. Other suitable anionic surfactants are 2,3-alkylsulfates, which are commercially available from Shell Oil Company under the name DAN<sup>®</sup>.

[0035] The sulfuric acid monoesters of linear or branched  $C_{7-21}$  alcohols ethoxylated with 1 to 6 mol of ethylene oxide, such as 2-methyl-branched  $C_{9-11}$  alcohols with an average of 3.5 mol of ethylene oxide (EO) or  $C_{12-18}$  fatty alcohols with 1 to 4 EO, are also suitable. Because of their high foaming ability, they are used in cleaning compositions only in relatively small amounts, for example in amounts of 1 to 5% by weight.

[0036] Further suitable anionic surfactants are the salts of alkylsulfosuccinic acids, which are also called sulfosuccinates or sulfosuccinic acid esters and represent the monoesters and/or diesters of sulfosuccinic acid with alcohols, preferably fatty alcohols and especially ethoxylated fatty alcohols. Preferred sulfosuccinates contain C<sub>8-18</sub> fatty alcohol radicals or mixtures thereof. Particularly preferred sulfosuccinates contain a fatty alcohol radical derived from ethoxylated fatty alcohols which themselves are non-ionic surfactants (see description below).

Sulfosuccinates whose fatty alcohol radicals are derived from ethoxylated fatty alcohols with a narrow distribution of homologues are in turn particularly preferred. Likewise, it is also possible to use alk(en)ylsuccinic acids preferably having 8 to 18 carbon atoms in the alk(en)yl chain, or salts thereof.

5 [0037] Other particularly suitable anionic surfactants are soaps. Suitable soaps are saturated fatty acid soaps, such as the salts of lauric acid, myristic acid, palmitic acid, stearic acid, hydrogenated erucic acid and behenic acid, and especially soap mixtures derived from natural fatty acids, e.g. coconut fatty acid, palm kernel fatty acid or tallow fatty acid.

10 [0038] The anionic surfactants, including the soaps, can be present in the form of their sodium, potassium or ammonium salts or in the form of soluble salts of organic bases such as monoethanolamine, diethanolamine or triethanolamine. The anionic surfactants are preferably present in the form of their sodium or potassium salts and especially in the form of the sodium salts.

15 [0039] The cleaning or detergent compositions according to the invention contain surfactants in an overall amount preferably of 5% by weight to 50% by weight, especially of 8% by weight to 30% by weight, based on the finished composition.

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[0040] The compositions according to the invention contain bleaching agents as a further component. If bleaching agents and bleach activator, if present, are contained in the form of so-called bleaching agent and/or bleach activator compounds, it has proved particularly advantageous for these particles containing bleaching agents and/or bleach activator to be at least partially provided with the protective layer described above, the particles preferably being coated to the extent of at least 65%. This prevents the relatively reactive bleaching agents from coming into contact with any other sensitive substances present, for example enzymes, destroying the activity of these substances and also losing at least part of their own activity.

[0041] Of the compounds that produce  $H_2O_2$  in water and are used as bleaching agents, sodium percarbonate, sodium perborate tetrahydrate and sodium perborate

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monohydrate are of particular importance. Examples of other bleaching agents which can be used are peroxopyrophosphates, citrate perhydrates and peracidic salts or per acids that produce H<sub>2</sub>O<sub>2</sub>, such as persulfates or persulfuric acid. A combination of sodium percarbonate with sodium sesquicarbonate is preferred particularly when the compositions according to the invention are used for washing textiles. If the compositions are used especially for cleaning hard surfaces, for example in dishwashing machines, they can also contain bleaching agents from the group comprising organic bleaching agents, if desired. Typical organic bleaching agents are diacyl peroxides, for example dibenzoyl peroxide. Other typical organic bleaching agents are peroxy acids, of which alkylperoxy acids and arylperoxy acids Preferred representatives are may be mentioned as particular examples. peroxybenzoic acid and its ring-substituted derivatives, such as alkylperoxybenzoic acids, but it is also possible to use peroxy-α-naphthoic acid and magnesium monoperphthalate, aliphatic or aliphatically substituted peroxy acids, such as acid, \(\epsilon\)-phthalimidoperoxycaproic acid, peroxystearic peroxylauric (phthalimidoperoxyhexanoic acid, PAP), ε-carboxybenzamidoperoxycaproic acid, N-nonenylamidoperadipic acid and N-nonenylamidopersuccinates, and aliphatic and araliphatic peroxydicarboxylic acids, such as 1,12-diperoxycarboxylic acid, diperoxybrassylic acid, acid, acid, diperoxysebacic 1,9-diperoxyazelaic N,Nacid and 2-decyldiperoxybutane-1,4-dioic diperoxyphthalic acids, terephthaloyldi(6-aminopercaproic acid).

[0042] To achieve an improved bleaching action when washing at temperatures of 60°C and below, and especially in the prewash, the compositions according to the invention can contain bleach activators. Bleach activators which can be used are compounds that yield aliphatic peroxocarboxylic acids preferably having 1 to 10 C atoms, especially 2 to 4 C atoms, and/or optionally substituted perbenzoic acid, under perhydrolysis conditions. Suitable substances are those carrying O-acyl and/or N-acyl groups having said number of C atoms, and/or optionally substituted benzoyl groups. Preference is given to polyacylated alkylenediamines, especially tetraacetylethylenediamine (TAED), acylated triazine derivatives, especially 1,5-

diacetyl-2,4-dioxohexahydro-1,3,5-triazine (DADHT), acylated glycolurils. especially 1,3,4,6-tetraacetylglycoluril (TAGU), N-acylimides, especially Nnonanoylsuccinimide (NOSI), acylated phenolsulfonates, especially n-nonanoyl- or isononanoyl-oxybenzenesulfonate (n- or iso-NOBS), acylated hydroxycarboxylic 5 acids, such as triethyl O-acetylcitrate (TEOC), carboxylic anhydrides, especially phthalic anhydride, isatoic anhydride and/or succinic anhydride, carboxamides, such as N-methyldiacetamide, glycolide, acylated polyhydric alcohols, especially triacetin, ethylene glycol diacetate, isopropenyl acetate, 2,5-diacetoxy-2,5dihydrofuran and the enol esters known from German patent applications 10 DE 196 16 693 and DE 196 16 767, as well as acetylated sorbitol and mannitol or their mixtures (SOR-MAN) described in European patent application EP 0 525 239, acylated sugar derivatives, especially pentaacetylglucose (PAG), pentaacetylfructose, tetraacetylxylose and octaacetyllactose, and acetylated, optionally N-alkylated glucamine or gluconolactone, triazole or triazole 15 derivatives, and/or particulate caprolactams and/or caprolactam derivatives, preferably N-acylated lactams, for example N-benzoylcaprolactam and Nacetylcaprolactam, which are known from international patent applications WO-A-94/27970, WO-A-94/28102, WO-A-94/28103, WO-A-95/00626, WO-A-95/14759 and WO-A-95/17498. The hydrophilically substituted acylacetals known from German patent application DE-A-196 16 769 and the acyllactams described in 20 German patent application DE-A-196 16 770 and international patent application WO-A-95/14075 are likewise preferably used. It is also possible to use the combinations of conventional bleach activators known from German patent application DE-A-44 43 177. Nitrile derivatives, such as cyanopyridines, nitrile quats and/or cyanamide derivatives, can also be used. Preferred bleach activators 25 are sodium 4-(octanoyloxy)benzenesulfonate, undecenoyloxybenzenesulfonate (UDOBS), sodium dodecanoyloxybenzenesulfonate (DOBS) and/or decanoyloxybenzoic acid (DOBA, OBC 10). If desired, such bleach activators are present in the conventional quantity range of 0.01 to 20% by weight, preferably in 30 amounts of 0.1 to 15% by weight, especially 1% by weight to 10% by weight,

based on the total composition.

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[0043] In addition to or instead of the conventional bleach activators, the compositions can also contain so-called bleach catalysts. These substances are bleach-reinforcing transition metal salts or transition metal complexes, for example Mn, Fe, Co, Ru or Mo salt complexes or carbonyl complexes. Mn, Fe, Co, Ru, Mo, Ti, V and Cu complexes with N-containing tripod ligands, and Co, Fe, Cu and Ru ammine complexes, are also suitable as bleach catalysts.

[0044] The content of bleaching agents in the compositions according to the invention is preferably 1 to 40% by weight and especially 10 to 20% by weight, it being particularly preferable to use perborate monohydrate and/or percarbonate.

[0045] The compositions according to the invention normally contain one or more builders, especially zeolites, silicates, carbonates, organic co-builders and, where their use is not prejudiced on ecological grounds - phosphates as well. The latter builders are preferably to be used particularly in cleaning compositions, such as cleaning tablets, for dishwashing machines.

[0046] Suitable crystalline sodium silicates in sheet form have the general formula  $NaMSi_xO_{2x+1}\cdot yH_2O$ , in which M is sodium or hydrogen, x is a number from 1.9 to 4 and y is a number from 0 to 20, preferred values of x being 2, 3 or 4. Preferred crystalline sheet silicates of the indicated formula are those in which M is sodium and x has a value of 2 or 3. Both  $\beta$  and  $\delta$  sodium disilicates,  $Na_2Si_2O_5\cdot yH_2O$ , are particularly preferred.

[0047] It is also possible to use amorphous sodium silicates with an Na<sub>2</sub>O:SiO<sub>2</sub> ratio of 1:2 to 1:3.3, preferably 1:2 to 1:2.8 and especially 1:2 to 1:2.6, which have delayed solubility and secondary washing properties. The delayed solubility compared with conventional amorphous sodium silicates can be brought about in a variety of ways, for example by surface treatment, compounding, compaction/densification or overdrying. Within the framework of the present invention, the term "amorphous" is also understood as meaning "X-amorphous". This means that, in X-ray diffraction experiments, the silicates do not exhibit the sharp X-ray reflections typical of crystalline substances, but rather at most one or more maxima

of the scattered X-radiation having a width of several degree units of the diffraction angle. However, it is even very possible to obtain particularly good builder properties when the silicate particles exhibit blurred or even sharp diffraction maxima in electron diffraction experiments. This is to be interpreted by saying that the products have microcrystalline regions with a size of 10 to a few hundred nm, values up to max. 50 nm and especially up to max. 20 nm being preferred. Densified/compacted amorphous silicates, compounded amorphous silicates and overdried X-amorphous silicates are particularly preferred.

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[0048] Finely crystalline, synthetic zeolite containing bound water is preferably zeolite A and/or P. A particularly preferred zeolite P is zeolite MAP<sup>®</sup> (commercial product from Crosfield), but zeolite X and mixtures of A, X and/or P are also suitable. Another example of a commercially available product which can preferably be used within the framework of the present invention is a co-crystallization product of zeolite X and zeolite A (approx. 80% by weight of zeolite X), which is marketed by CONDEA Augusta S.p.A. under the registered trade mark VEGOBOND AX<sup>®</sup> and can be described by the formula

$$nNa_2O \cdot (1-n)K_2O \cdot Al_2O_3 \cdot (2-2.5)SiO_2 \cdot (3.5-5.5)H_2O$$

Suitable zeolites have a mean particle size of less than 10 μm (volume distribution; measurement method: Coulter Counter) and contain preferably 18 to 22% by weight, especially 20 to 22% by weight, of bound water.

[0049] It is also possible to use the generally known phosphates as builders, provided that their use is not to be avoided on ecological grounds. Of the large number of commercially available phosphates, the alkali metal phosphates are of the greatest importance in the detergent and cleaning composition industry, pentasodium or pentapotassium triphosphate (sodium or potassium tripolyphosphate) being particularly preferred. "Alkali metal phosphates" is the generalized term used to describe the alkali metal (especially sodium and potassium) salts of the various phosphoric acids, which can be subdivided into metaphosphoric acids,

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(HPO<sub>3</sub>)<sub>n</sub>, and orthophosphoric acid, H<sub>3</sub>PO<sub>4</sub>, as well as higher-molecular representatives. Phosphates offer a combination of several advantages: They act as alkali carriers, prevent limescale deposits on machine parts and limescale encrustations in fabrics, and also contribute to the cleaning efficiency. Sodium dihydrogenphosphate, NaH<sub>2</sub>PO<sub>4</sub>, exists as the dihydrate (density: 1.91 g.cm<sup>-3</sup>, melting point: 60°) and the monohydrate (density: 2.04 g.cm<sup>-3</sup>). Both salts are very readily water-soluble, white powders which lose the water of crystallization on change into the weakly acidic diphosphate (disodium and hydrogendiphosphate, Na<sub>2</sub>H<sub>2</sub>P<sub>2</sub>O<sub>7</sub>) at 200°C and into sodium trimetaphosphate (Na<sub>3</sub>P<sub>3</sub>O<sub>9</sub>) and Madrell's salt (see below) at higher temperature. NaH<sub>2</sub>PO<sub>4</sub> gives an acidic reaction; it is formed when phosphoric acid is adjusted to a pH of 4.5 with hydroxide solution and the mash is sprayed. Potassium sodium dihydrogenphosphate (primary or monobasic potassium phosphate, potassium biphosphate, KDP), KH<sub>2</sub>PO<sub>4</sub>, is a white salt which has a density of 2.33 g.cm<sup>-3</sup> and a melting point of 253° [decomposition with the formation of potassium polyphosphate, (KPO<sub>3</sub>)<sub>x</sub>] and is readily soluble in water. Disodium hydrogenphosphate (secondary sodium phosphate), Na<sub>2</sub>HPO<sub>4</sub>, is a very readily water-soluble, colourless crystalline salt. It exists in anhydrous form and with 2 mol of water (density: 2.066 g.cm<sup>-3</sup>, water loss at 95°), 7 mol of water (density: 1.68 g.cm<sup>-3</sup>, melting point: 48° with loss of 5H<sub>2</sub>O) and 12 mol of water (density: 1.52 g.cm<sup>-3</sup>, melting point: 35° with loss of 5H<sub>2</sub>O), becomes anhydrous at 100° and changes into the diphosphate, Na<sub>4</sub>P<sub>2</sub>O<sub>7</sub>, on stronger heating. Disodium hydrogenphosphate is prepared by neutralizing phosphoric acid with sodium carbonate solution using phenolphthalein as indicator. Dipotassium hydrogenphosphate (secondary or dibasic potassium phosphate), K<sub>2</sub>HPO<sub>4</sub>, is a readily watersoluble, amorphous white salt. Trisodium phosphate (tertiary sodium phosphate), Na<sub>3</sub>PO<sub>4</sub>, takes the form of colourless crystals which as the dodecahydrate have a density of 1.62 g.cm<sup>-3</sup> and a melting point of 73-76°C (decomposition), as the decahydrate (corresponding to 19-20% of P2O5) have a melting point of 100°C and in anhydrous form (corresponding to 39-40% of P<sub>2</sub>O<sub>5</sub>) have a density of 2.536 5

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g.cm<sup>-3</sup>. Trisodium phosphate is readily soluble in water to give an alkaline reaction and is prepared by evaporating a solution of exactly 1 mol of disodium phosphate and 1 mol of NaOH. Tripotassium phosphate (tertiary or tribasic potassium phosphate), K<sub>3</sub>PO<sub>4</sub>, is a deliquescent, white granular powder which has a density of 2.56 g.cm<sup>-3</sup> and a melting point of 1340° and is readily soluble in water to give an alkaline reaction. It is formed e.g. on heating Thomas slag with coal and potassium sulfate. Despite their higher price, the more readily soluble and hence highly effective potassium phosphates are frequently preferred to the corresponding sodium compounds in the cleaning composition industry. Tetrasodium diphosphate (sodium pyrophosphate), Na<sub>4</sub>P<sub>2</sub>O<sub>7</sub>, exists in anhydrous form (density: 2.534 g.cm<sup>-3</sup>, melting point: 988°, also given as 880°) and as the decahydrate (density: 1.815-1.836 g.cm<sup>-3</sup>, melting point: 94° with water loss). Both substances are colourless crystals that dissolve in water to give an alkaline reaction. Na<sub>4</sub>P<sub>2</sub>O<sub>7</sub> is formed by heating disodium phosphate to >200° or by reacting phosphoric acid with sodium carbonate in stoichiometric proportions and dehydrating the solution by spraying. The decahydrate complexes heavy metal salts and hardness constituents and hence reduces the hardness of the water. Potassium diphosphate (potassium pyrophosphate), K<sub>4</sub>P<sub>2</sub>O<sub>7</sub>, exists in the form of the trihydrate and is a water-soluble, colourless hygroscopic powder having a density of 2.33 g.cm<sup>-3</sup>, the pH of a 1% solution at 25° being 10.4. NaH<sub>2</sub>PO<sub>4</sub> and KH<sub>2</sub>PO<sub>4</sub> condense to form higher-molecular sodium and potassium phosphates, which can be subdivided into cyclic representatives, namely sodium and potassium metaphosphates, and types in the form of chains, namely sodium and potassium polyphosphates. A large number of names are used for the latter in particular: fused or calcined phosphates, Graham's salt, Kurroll's salt and Madrell's salt. All higher sodium and potassium phosphates have the common designation of condensed phosphates. The technically important pentasodium triphosphate,  $Na_5P_3O_{10}$ (sodium tripolyphosphate), is a non-hygroscopic, water-soluble, white salt of the general formula  $NaO-[P(O)(ONa)-O]_n-Na$ , where n=3, which is anhydrous or crystallizes with 6H<sub>2</sub>O. About 17 g of the salt free of water of crystallization dissolve in 100 g

of water at room temperature, approx. 20 g dissolve at 60° and around 32 g dissolve at 100°; after the solution has been heated at 100° for two hours, about 8% of orthophosphate and 15% of diphosphate form due to hydrolysis. To prepare pentasodium triphosphate, phosphoric acid is reacted in stoichiometric proportions with sodium carbonate solution or sodium hydroxide solution, and the resulting solution is dehydrated by spraying. Similarly to Graham's salt and sodium diphosphate, pentasodium triphosphate dissolves many insoluble metal compounds (including lime soaps etc.). Pentapotassium triphosphate,  $K_5P_3O_{10}$  (potassium tripolyphosphate), is marketed e.g. in the form of a 50% by weight solution (>23% of  $P_2O_5$ , 25% of  $K_2O$ ). Potassium polyphosphates are widely used in the detergent and cleaning composition industry. Sodium potassium tripolyphosphates also exist and these can likewise be used within the framework of the present invention. They are formed e.g. when sodium trimetaphosphate is hydrolysed with KOH:

$$(NaPO_3)_3 + 2KOH \rightarrow Na_3K_2P_3O_{10} + H_2O$$

[0050] According to the invention, these can be used in exactly the same way as sodium tripolyphosphate, potassium tripolyphosphate or mixtures of the two; it is also possible according to the invention to use mixtures of sodium tripolyphosphate and sodium potassium tripolyphosphate, mixtures of potassium tripolyphosphate and sodium potassium tripolyphosphate or mixtures of sodium tripolyphosphate, potassium tripolyphosphate and sodium potassium tripolyphosphate.

[0051] Organic co-builders which can be used in particular in the compositions according to the invention are polycarboxylates/polycarboxylic acids, polymeric polycarboxylates, aspartic acid, polyacetals, dextrins, other organic co-builders and phosphonates. These classes of substances are described below.

[0052] Examples of organic builders which can be used are polycarboxylic acids in the form of their sodium salts, polycarboxylic acids being understood as meaning carboxylic acids carrying more than one acid group. Examples of these

are citric acid, adipic acid, succinic acid, glutaric acid, malic acid, tartaric acid, maleic acid, fumaric acid, sugar acids, aminocarboxylic acids and nitrilotriacetic acid (NTA), provided that there are no objections to their use on ecological grounds, as well as mixtures of said acids. Preferred salts are those of polycarboxylic acids such as citric acid, adipic acid, succinic acid, glutaric acid, tartaric acid, sugar acids and mixtures thereof.

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[0053] It is also possible to use the acids per se. Apart from their action as builders, the acids typically have the property of an acidifying component and thus serve also to adjust detergent or cleaning compositions to a lower and milder pH. Acids which may be mentioned in particular here are citric acid, succinic acid, glutaric acid, adipic acid, gluconic acid and any desired mixtures thereof.

[0054] Other suitable builders are polymeric polycarboxylates, for example the alkali metal salts of polyacrylic acid or polymethacrylic acid, such as those with a relative molecular weight of 500 to 70,000 g/mol.

[0055] In terms of the present specification, the molecular weights indicated for polymeric polycarboxylates are weight-average molecular weights, M<sub>w</sub>, of the corresponding acid form, which were determined in principle by means of gel permeation chromatography (GPC) using a UV detector. Measurement was made against an external polyacrylic acid standard that gives realistic molecular weight values by virtue of its structural relationship to the polymers under investigation. These data are markedly different from the molecular weight data obtained using polystyrenesulfonic acids as the standard. The molecular weights measured against polystyrenesulfonic acids are normally markedly higher than those indicated in the present specification.

25 [0056] Particularly suitable polymers are polyacrylates preferably having a molecular weight of 2000 to 20,000 g/mol. Because of their superior solubility, short-chain polyacrylates having molecular weights of 2000 to 10,000 g/mol, particularly preferably 3000 to 5000 g/mol, are in turn preferable within this group. [0057] Other suitable polymers are copolymeric polycarboxylates, especially copolymers of acrylic acid with methacrylic acid and copolymers of acrylic acid or

methacrylic acid with maleic acid. Copolymers of acrylic acid with maleic acid which contain 50 to 90% by weight of acrylic acid and 50 to 10% by weight of maleic acid have proved particularly suitable. Their relative molecular weight, based on the free acids, is generally 2000 to 70,000 g/mol, preferably 20,000 to 50,000 g/mol and especially 30,000 to 40,000 g/mol.

[0058] The (co)polymeric polycarboxylates can be used either as a powder or as an aqueous solution. The content of (co)polymeric polycarboxylates in the compositions is preferably 0.5 to 20% by weight, especially 3 to 10% by weight.

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[0059] To improve the water solubility, the polymers can also contain allylsulfonic acids, for example allyloxybenzenesulfonic acid and methallylsulfonic acid, as monomers.

[0060] Particular preference is also given to biodegradable polymers consisting of more than two different monomer units, for example those which contain salts of acrylic acid and maleic acid together with vinyl alcohol or vinyl alcohol derivatives, or salts of acrylic acid and a 2-alkylallylsulfonic acid together with sugar derivatives, as monomers.

[0061] Other preferred copolymers are those which preferably contain acrolein and acrylic acid/acrylic acid salts or acrolein and vinyl acetate as monomers.

[0062] Similarly, other preferred builders which may be mentioned are polymeric aminodicarboxylic acids, their salts or their precursors. Polyaspartic acids or their salts and derivatives are particularly preferred.

[0063] Other suitable builders are polyacetals obtainable by reacting dialdehydes with polyolcarboxylic acids having 5 to 7 C atoms and at least 3 hydroxyl groups. Preferred polyacetals are obtained from dialdehydes such as glyoxal, glutaraldehyde, terephthalaldehyde and mixtures thereof, and polyolcarboxylic acids such as gluconic acid and/or glucoheptonic acid.

[0064] Other suitable organic builders are dextrins, for example carbohydrate oligomers or polymers obtainable by the partial hydrolysis of starches. The hydrolysis can be carried out by conventional processes, for example acid-catalysed or enzyme-catalysed processes. Preferred hydrolysis products are those with

average molecular weights ranging from 400 to 500,000 g/mol. A polysaccharide with a dextrose equivalent (DE) ranging from 0.5 to 40, especially 2 to 30, is preferred, DE being a conventional measure of the reducing action of a polysaccharide compared with dextrose, which has a DE of 100. It is also possible to use maltodextrins with a DE of between 3 and 20 and dry glucose syrups with a DE of between 20 and 37, as well as so-called yellow dextrins and white dextrins with higher molecular weights ranging from 2000 to 30,000 g/mol. The oxidized derivatives of such dextrins are their reaction products with oxidizing agents that are capable of oxidizing at least one alcohol group of the saccharide ring to a carboxylic acid group. An oxidized oligosaccharide is also suitable and a product oxidized on C<sub>6</sub> of the saccharide ring can be particularly advantageous.

[0065] Further suitable co-builders are oxydisuccinates and other disuccinate derivatives, preferably ethylenediaminedisuccinate. Ethylenediamine-N,N'-disuccinate (EDDS) is used here, preferably in the form of its sodium or magnesium salts. Preference is also given in this connection to glyceroldisuccinates and glyceroltrisuccinates. Suitable doses are 3 to 15% by weight in formulations containing zeolites and/or silicates.

[0066] Examples of other organic co-builders which can be used are acetylated hydroxycarboxylic acids or their salts, which can optionally also be in the form of lactones and have at least 4 carbon atoms, at least one hydroxyl group and at most two acid groups.

[0067] Another class of substances with co-builder properties is phosphonates, particularly hydroxyalkanephosphonates or aminoalkanephosphonates. Of the hydroxyalkanephosphonates, 1-hydroxyethane-1,1-diphosphonate (HEDP) is of particular importance as a co-builder. It is preferably used as a sodium salt, the disodium salt giving a neutral reaction and the tetrasodium salt an alkaline reaction (pH 9). Suitable aminoalkanephosphonates are preferably ethylenediaminetetramethylenephosphonate (EDTMP), diethylenetriaminepentamethylenephosphonate (DTPMP) and their higher homologues. They are preferably used in the form of the sodium salts giving a neutral reaction, e.g. as the hexasodium salt of EDTMP or

as the heptasodium or octasodium salt of DTPMP. Within the phosphonate class, it is preferable to use HEDP as a builder. Aminoalkanephosphonates additionally have a pronounced binding capacity for heavy metals. Accordingly, it may be preferable, especially if the compositions also contain bleach, to use aminoalkanephosphonates, especially DTPMP, or mixtures of said phosphonates.

[0068] It is further possible for any compounds that are capable of forming complexes with alkaline earth metal ions to be used as co-builders.

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[0069] As additional conventional ingredients, the detergent and cleaning composition according to the invention can contain particularly enzymes, sequestering agents, electrolytes, pH regulators and other auxiliary substances, such as greying inhibitors, colour migration inhibitors, foam regulators, additional bleach activators, dyestuffs and perfumes.

[0070] By virtue of the protective layer applied according to the invention, enzymes and bleaching agents can be present in the composition simultaneously without their activity decreasing substantially, even on prolonged storage.

[0071] Suitable enzymes which can be used in the compositions belong to the class comprising oxidases, proteases, lipases, cutinases, amylases, pullulanases, cellulases, hemicellulases, xylanases and peroxidases, as well as mixtures thereof, for example proteases such as BLAP®, Optimase®, Opticlean®, Maxacal®, Maxaperm®, Alcalase®, Esperase® and/or Savinase®, amylases such as Termamyl®, Amylase-LT®, Maxamyl®, Duramyl® and/or Purafect® OxAm, lipases such as Lipolase®, Lipomax®, Lumafast® and/or Lipozyme®, and cellulases such as Celluzyme® and/or Carezyme®. Particularly suitable enzymatic ingredients are those obtained from fungi or bacteria, such as Bacillus subtilis, Bacillus licheniformis, Streptomyces griseus, Humicola lanuginosa, Humicola insolens, Pseudomonas pseudoalcaligenes or Pseudomonas cepacia. The enzymes, if used, can be adsorbed on carriers and/or embedded in sheathing substances, for example as described in European patent EP 0 564 476 or international patent application WO 94/23005, in order to protect them from premature inactivation. They are present in the surfactant mixtures according to the invention preferably in amounts

of up to 10% by weight, especially 0.2% by weight to 2% by weight, it being particularly preferable to use enzymes stabilized against oxidative degradation.

[0072] It can be advantageous, especially for use in mechanical washing or cleaning processes, to add conventional foam inhibitors to the compositions. Examples of suitable foam inhibitors are soaps of natural or synthetic origin which contain a high proportion of C<sub>18</sub>-C<sub>24</sub> fatty acids. Examples of suitable non-surfactant foam inhibitors are organopolysiloxanes and mixtures thereof with microfine, optionally silanized silicic acid, as well as paraffins, waxes, microcrystalline waxes and mixtures thereof with silanized silicic acid or bistearylethylenediamide. It is also advantageous to use mixtures of different foam inhibitors, for example mixtures of silicones, paraffins or waxes. The foam inhibitors, especially those containing silicones or paraffins, are preferably bound to a water-soluble or water-dispersible, granular carrier, mixtures of paraffins and bistearylethylenediamides being particularly preferred.

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15 **[0073]** The polyphosphonic acid salts used, in amounts of 0.1 to 1.5% by weight, are preferably the sodium salts, giving a neutral reaction, of e.g. 1-hydroxyethane-1,1-diphosphonate, diethylenetriaminepentamethylenephosphonate or ethylenediaminetetramethylenephosphonate.

[0074] If the composition according to the invention is used as a so-called heavy-duty detergent, it preferably contains from 3 to 30% by weight of anionic surfactants, 2 to 20% by weight of non-ionic surfactants, 10 to 50% by weight of builders, 5 to 25% by weight of bleaching agents, 1 to 10% by weight of bleach activators, 0.3 to 3% by weight of enzymes, 0.3 to 8% by weight of co-builders and 0.1 to 6% by weight of defoaming agents.

25 [0075] The detergent and cleaning compositions according to the invention take the form of solid particles, especially powders, granules, extrudates or mouldings (called tablets). The invention also encompasses particles that are at least partially provided with a protective layer and are processed to granules, extrudates or mouldings in a subsequent processing stage. The individual forms can be produced by processes known from the state of the art.

[0076] The protective layer can be applied e.g. in the fluidizing apparatus described in DE 196 44 244. Preferably, aqueous solutions or dispersions or melts of the sheathing substances are sprayed onto the particulate compositions to be coated. In one possible embodiment, the sheathing substance is applied in the form of its melt in a fluidized bed apparatus. Preferably, the molten sheathing substance, kept at a temperature at least 20°C above the melting point, is sprayed with atomizing air, which is at least at the same temperature, through nozzles into the fluidizing chamber filled with the particles to be coated, the outer jacket of the chamber being kept at a temperature of 20 to 50°C, preferably at most 40°C. The atomizing air can additionally serve to heat the feed channel for the melt.

## **Claims**

- Particulate detergent and cleaning composition containing surfactants,
   bleaching agents and optionally other conventional ingredients,
   characterized in that the particles are at least partially provided with a protective layer.
- 2. Composition according to Claim 1, characterized in that at least 65% of the particles are coated.
  - 3. Composition according to Claim 1 or 2, characterized in that the protective layer has a thickness of 0.1  $\mu m$  to 100  $\mu m$ .
- 15 4. Composition according to one of Claims 1 to 3, characterized in that the protective layer contains 50% by weight to 100% by weight of water-soluble organic substances or mixtures of substances melting in the range from 40°C to 200°C.
- 20 5. Composition according to Claim 4, characterized in that the water-soluble substance, solid at room temperature, is a linear primary saturated or unsaturated alcohol having 16 to 22 C atoms, etherified with an average of 45 to 120, especially 60 to 110, mol equivalents of ethylene oxide, an ethoxylated fatty acid, an ethoxylated fatty acid amide, an ethoxylation product of hydroxy fatty acid esters having 1 to 6 C atoms in the alcohol moiety of the ester, the degree of ethoxylation in each case being especially 45 to 120, or a mixture of these compounds.
- 6. Composition according to one of Claims 1 to 5, characterized in that the protective layer contains up to 10% by weight of water-insoluble inorganic

components.

organic dyestuff.

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7. Composition according to one of Claims 1 to 6, characterized in that the protective layer contains up to 10% by weight of flowability improvers.

8. Composition according to one of Claims 1 to 6, characterized in that the protective layer consists of a sheathing system containing 45% by weight to 100% by weight of a water-soluble organic substance solid at room temperature and melting in the range from 40°C to 200°C, up to 10% by weight, preferably up to 5% by weight and especially 0.5% by weight to 5% by weight of a finely divided, water-insoluble inorganic pigment, up to 20% by weight, preferably up to 10% by weight and especially 1% by weight to 5% by weight of a flowability improver and up to 1.5% by weight of an

9. Composition according to Claim 8, characterized in that the sheathing system contains small amounts of a compound of general formula I:

 $R[O(C_nH_{2n}O)_mH]_x (I)$ 

in which R is an organic radical having 3 to 12 C atoms, especially 4 to 10 C atoms, n is 2 or 3, m is 1 to 15 and x is 2 or 3.

10. Composition according to Claim 9, characterized in that the compounds of formula I are prepared by reacting alcohols R[OH]<sub>x</sub> with ethylene oxide and/or propylene oxide and contain both ethoxy groups (n = 2) and 1,2-propoxy groups (n = 3), the average number of ethoxy groups per hydroxyl group of the alcohol R[OH]<sub>x</sub> preferably being up to 10 and the average number of propoxy groups per hydroxyl group of the alcohol R[OH]<sub>x</sub> preferably being up to 5.

- 11. Composition according to Claim 9 or 10, characterized in that the compound of general formula I is present in an amount of 4% by weight to 8% by weight.
- 5 12. Composition according to one of Claims 1 to 11, characterized in that it contains builders, enzymes, sequestering agents, electrolytes, pH regulators and other auxiliary substances, such as greying inhibitors, colour migration inhibitors, foam regulators, bleach activators, dyestuffs and perfumes.
- 10 13. Process for the preparation of detergent and cleaning compositions containing surfactants and bleaching agents, optionally together with other conventional ingredients, characterized in that a protective layer is applied to the compositions or parts thereof.
- 15 14. Process according to Claim 13, characterized in that the sheathing substance used for the protective layer is applied in the form of its melt in a fluidized bed apparatus.
- substance, kept at a temperature at least 20°C above the melting point, is sprayed with atomizing air, which is at least at the same temperature, through nozzles into the fluidizing chamber filled with the particles to be coated, the outer jacket of the chamber being kept at a temperature of 20°C to 50°C, preferably at most 40°C.